



HAL
open science

Detailed kinetic modeling of the formation of toxic polycyclic aromatic hydrocarbons (PAHs) coming from pyrolysis in low-pressure gas carburizing conditions

Tsilla Bensabath, Hubert Monnier, Pierre-Alexandre Glaude

► To cite this version:

Tsilla Bensabath, Hubert Monnier, Pierre-Alexandre Glaude. Detailed kinetic modeling of the formation of toxic polycyclic aromatic hydrocarbons (PAHs) coming from pyrolysis in low-pressure gas carburizing conditions. *Journal of Analytical and Applied Pyrolysis*, 2016, 122, pp.342-354. <10.1016/j.jaap.2016.09.007>. <hal-01510237>

HAL Id: hal-01510237

<https://hal.science/hal-01510237v1>

Submitted on 19 Apr 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Title: Detailed kinetic modeling of the formation of toxic polycyclic aromatic hydrocarbons (PAHs) coming from pyrolysis in low-pressure gas carburizing conditions

Authors:

Tsilla Bensabath^{a,b} (tsilla.bensabath@univ-lorraine.fr)

Hubert Monnier^b (hubert.monnier@inrs.fr)

Pierre-Alexandre Glaude^a (pierre-alexandre.glaude@univ-lorraine.fr)

Affiliations:

^aLaboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, 1, rue Grandville, 54000 Nancy, France

^bInstitut National de Recherche et de Sécurité, 1, rue du Morvan, 54519 Vandœuvre-lès-Nancy, France

Abstract:

Hydrocarbon pyrolysis in low-pressure gas carburizing conditions leads to gas phase reactions, which produce polycyclic aromatic hydrocarbons (PAHs), some of which, such as benzo[*a*]pyrene, are carcinogenic. Workers can be exposed to these PAHs during maintenance and cleaning operations of carburizing furnaces. The aim of the study is the prediction of the formation of sixteen PAHs considered as priority pollutants by the Environmental Protection Agency in the United States (US EPA). A model has been implemented in order to describe the reaction pathways leading to their formation. It was validated using experimental data from the literature, obtained during pyrolysis of different hydrocarbons such as acetylene and ethylene. Flux analyses were realized in order to determine main reaction pathways leading to benzene depending on the reactant. Simulations were also performed to compare PAH formation between acetylene, ethylene and propane pyrolysis.

Keywords: PAHs; benzo[*a*]pyrene; low-pressure gas carburizing; kinetic model; hydrocarbon pyrolysis

1 **1. Introduction**

2 Low-pressure gas carburizing is a heat treatment process used to harden surface of steel by
3 enriching the metal with carbon atoms coming from pyrolysis of hydrocarbons. This process is used to
4 avoid wear of pieces subjected to strong constraints [1]. Unfortunately, in the same time, a wide
5 variety of molecules and radicals are formed in the gas phase, which lead to the formation of
6 polycyclic aromatic hydrocarbons (PAHs), which are soot precursors [2]. PAHs are toxic and some of
7 them are known carcinogens [3]. This is the case of benzo[*a*]pyrene (B[*a*]P), which is used as a
8 reference for assessing the carcinogenicity of other PAHs through the Toxic Equivalency Factor (TEF)
9 [4]. Workers can be exposed to these substances by inhalation and skin contact during maintenance
10 and cleaning operations of carburizing furnaces [5]. Sixteen PAHs, containing two to six carbon atom
11 rings, have been classified as priority pollutants by the Environmental Protection Agency in the United
12 States (EPA-PAHs) [6]. Understanding PAH formation is important to make safer and cleaner low-
13 pressure gas carburizing processes, as other processes which can produce PAHs by hydrocarbon
14 pyrolysis, such as atmosphere carburizing and carbonitriding, or by combustion.

15 There are two main pathways for the formation of the first aromatic rings, i.e. benzene and
16 phenyl radical, which are the main actors of PAH growth [7,8]. The former, the C₂ – C₄ pathway,
17 consists of the addition on an acetylene molecule of a C₄H₅ radical yielding benzene and of a C₄H₃
18 radical yielding a phenyl radical [9]. However, Miller and Melius estimated that this way cannot be the
19 only responsible for the first ring formation [10]. They proposed the C₃ – C₃ pathway, which consists
20 of the reaction between two propargyl radicals. Several studies focused on this reaction [11,12].
21 Cyclopentadienyl radicals also play an important role. They account for naphthalene formation by self-
22 combination [13–15] and, in a similar way, in the formation of other PAHs such as phenanthrene [16].

23 Although the reactions which lead to the formation of benzene are well known today, the same
24 cannot be said of the reactions responsible for the formation of heavier PAHs [8,17]. PAH growth
25 results from various reaction pathways in competition. The best known is the Hydrogen Abstraction
26 C₂H₂ Addition (HACA) mechanism presented by Frenklach et al. [18]. It consists in the elimination of
27 a hydrogen atom from the initial PAH by an H-atom abstraction reaction, followed by the addition on
28 the obtained radical site of an acetylene molecule. This mechanism is an important pathway because of

29 its low energy barrier and high exothermicity [19]. Other mechanisms were considered. Among them,
30 there are the combinative growth mechanism, which consists in the growth of a PAH by adding
31 aromatic rings, the cyclopentadienyl radical recombination [20] and the Hydrogen Abstraction Vinyl
32 Addition (HAVA) mechanism [21]. Another possible pathway is the Diels-Alder mechanism but it is
33 not competitive with the HACA mechanism [22].

34 Various models were developed in order to describe reactions, which occur during
35 hydrocarbon combustion or pyrolysis up to the formation of PAHs. Frenklach et al. developed a model
36 for acetylene and ethylene flames, which describes PAH growth up to molecules involving four
37 aromatic rings and soot formation [7,23]. Slavinskaya et al. worked on a model for methane and
38 ethylene flames and described PAH growth up to five aromatic rings [17,24]. Their model also allows
39 an estimation of the amount of soot. Saggese et al. studied acetylene pyrolysis thanks to a model which
40 combines a gas phase mechanism including PAH growth up to four aromatic rings and soot precursors
41 with a soot formation mechanism [25]. More recently, Wang et al. published a model for propene
42 pyrolysis [26] based on a model for ethane pyrolysis [27]. They did not describe the formation of
43 heavy species (containing more than twelve carbon atoms) but emphasized the formation of first rings
44 (benzene, styrene, naphthalene). In conditions close to low-pressure gas carburizing, Ziegler et al.
45 proposed a model for Chemical Vapor Deposition (CVD) by propane pyrolysis, which takes into
46 account PAH formation up to four aromatic rings [28,29]. The model which considers the heaviest
47 PAHs is the model of Norinaga et al. It details PAH formation up to coronene, involving seven
48 aromatic rings. It was validated for ethylene, acetylene and propylene pyrolysis in CVD conditions
49 [30–32], as for propane pyrolysis [33]. Lastly, a model by Matsugi and Miyoshi [34], following
50 studies of pyrolysis of mono-aromatics such as toluene [35,36], highlighted other reaction pathways to
51 PAHs, such as the Phenyl Addition and Cyclization (PAC) mechanism.

52 This study aims to develop a model of hydrocarbon pyrolysis in gas carburizing conditions,
53 i.e. at low pressure and at temperature ranging from 1173 to 1323 K [1,37], but without taking into
54 account the presence of steel pieces. It focuses on the formation of the sixteen EPA-PAHs, which are
55 not all modeled up to now in available mechanisms. These target PAHs are: naphthalene,
56 acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene,

57 benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene,
58 indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene and benzo[*ghi*]perylene. They are represented in
59 Supplementary data (S1). The design of the model is detailed in section 2. Its validation was realized
60 with experimental data from the literature.

61 Few experimental data on the sixteen EPA-PAHs in pyrolysis are available. Sánchez et al.
62 quantified them at the outlet of a plug-flow reactor in the case of acetylene and ethylene pyrolysis [38–
63 41]. They worked at different temperatures between 873 and 1323 K and at atmospheric pressure with
64 a diluted reactant. At low pressure (undiluted reactant), Norinaga et al. measured thirteen EPA-PAHs
65 during acetylene, ethylene and propylene pyrolysis in a plug-flow reactor at 1173 K [42]. Ziegler et al.
66 pyrolysed propane in a perfectly stirred reactor at 2.7 kPa and at different temperatures between 1173
67 and 1323 K [28,29]. Only PAHs up to pyrene were experimentally quantified. All these data were used
68 in the model development. In this study, simulations will be presented for acetylene and ethylene
69 pyrolysis in the operating conditions of Norinaga et al. and of Sánchez et al.

70

71 **2. Modeling**

72 A detailed kinetic model for the pyrolysis of light hydrocarbons, such as acetylene, ethylene
73 and propane, and PAH growth has been developed, based on a model for the combustion of aromatic
74 compounds validated in particular in the case of combustion of ethylbenzene [43] and anisole [44].
75 The initial mechanism contained the reactions of pyrolysis and oxidation of many hydrocarbons, the
76 reactions producing the first aromatic rings from lighter species by C₂ – C₄ pathway [45], C₃ – C₃
77 pathway [46] and cyclopentadienyl radicals [47], and the reactions of formation of PAHs up to four
78 aromatic rings especially by the HACA mechanism [48]. Pressure dependence of rate constants is
79 taken into account when available. This model has been simplified by removing all oxidation reactions
80 and all species containing oxygen atoms. It has been completed with reactions for the production of
81 heavier PAHs up to seven aromatic rings. Missing reactions have been added and some kinetic
82 constants have been updated to take into account pathways, which could be negligible in oxidation
83 conditions. The most important changes are detailed in this section. For all the reactions added,
84 thermodynamic data of the compounds not present in the initial mechanism have been evaluated by the

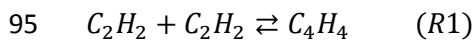
85 software THERGAS [49] based on Benson's group additivity method or by analogy with isomers. The
86 final model contains 358 species and 1245 reactions. It is available in Supplementary data. In the
87 following, the observations about model predictions are made compared to the experimental data of
88 Norinaga and Deutschmann for acetylene and ethylene pyrolysis [31]. Species which appear in
89 reactions (R1) to (R20) are represented in Supplementary data (S2).

90

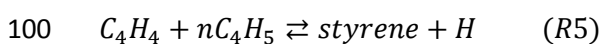
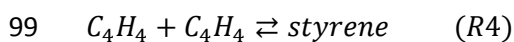
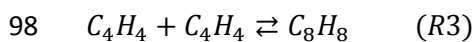
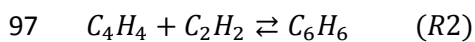
91 2.1. Reactant consumption and first steps of pyrolysis

92 Regarding acetylene pyrolysis, the model [44] overestimated the consumption of acetylene
93 (C_2H_2) as the production of vinylacetylene (C_4H_4), the main primary product of acetylene [50].

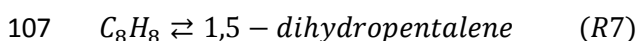
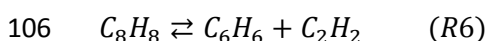
94 Reaction (R1), which was irreversible and thereby too fast, has been set reversible:



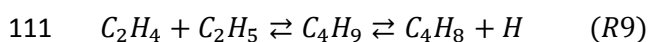
96 Other reactions of vinylacetylene have been added:



101 where C_6H_6 , C_8H_8 and nC_4H_5 represent benzene, 1,3,5,7-cyclooctatetraene and 1,3-butadienyl radical,
102 respectively. Kinetic coefficients used for reactions (R2) and (R3) are those proposed by Norinaga et
103 al. [32] and those used for reactions (R4) and (R5) are from Slavinskaya and Frank [17]. Reactions of
104 consumption of 1,3,5,7-cyclooctatetraene have been added with kinetic coefficients proposed by
105 Dudek et al. [51]. They lead to the formation of benzene and styrene:



109 As to ethylene pyrolysis, the model underestimated the experimental consumption of ethylene
110 (C_2H_4). A new pathway of consumption has been added with kinetic coefficients from Curran [52]:



112 where C_2H_5 , C_4H_9 and C_4H_8 represent ethyl radical, butyl radical and 1-butene, respectively.

113 Moreover, the reaction rate of the H-atom abstraction of ethylene by a hydrogen atom to produce a
114 vinyl radical has a large influence on ethylene consumption. The rate constant of this reaction has
115 therefore been updated with data of Wang and Frenklach [7].

116

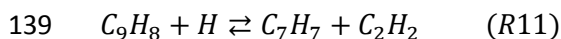
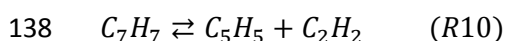
117 2.2. Formation of first rings

118 The description of the evolution of first cyclic species containing five or six carbon atoms is
119 essential because these rings are the basis of PAH formation. Some new reaction pathways for benzene
120 and styrene formation have been presented in section 2.1 (reactions (R2) to (R8)). Reaction (R2) is an
121 important reaction pathway for benzene formation in acetylene pyrolysis, especially at temperatures
122 lower than 1200 K [25]. Flux analysis shows that reaction (R3) consumes more vinylacetylene than
123 reaction (R4), even if this tendency is less pronounced when temperature increases. 1,3,5,7-
124 cyclooctatetraene produced by (R3) is overwhelmingly converted through reaction (R6) to benzene,
125 which is one of the main source of styrene. So, ultimately, both reactions (R3) and (R4) contribute to
126 the formation of styrene during acetylene pyrolysis. When temperature increases, the part of reaction
127 (R4) increases for short residence times (47% at 1073K and 54% at 1173K for $\tau = 0.24$ s) but
128 decreases for longer residence times (47% at 1073K and 28% at 1173K for $\tau = 1$ s).

129 Two other reaction pathways have been added to the model, leading to benzene and to
130 cyclopentadiene, respectively. They come from a theoretical study of Cavallotti et al. [53] about
131 reactions of 1,3-butadiene with vinyl radical (scheme S3). Kinetic coefficients are those proposed by
132 these authors. The addition of these reactions is especially sensitive in prediction of 1,3-butadiene and
133 benzene and thereby of most heavier aromatic compounds during ethylene pyrolysis.

134 A reaction pathway to indene (C_9H_8) from cyclopentadienyl radical (C_5H_5) via benzyl radical
135 (C_7H_7) by successive additions of acetylene molecules has also been added. Several studies on this

136 pathway exist in the literature even if the intermediate C_7H_7 is not necessarily benzyl radical [54–56].
137 Two reactions, (R10) and (R11), have been set reversible and updated:



140 Kinetic coefficients of reaction (R11) have been modified based on the theoretical study of Kislov and
141 Mebel [57]. This study details the intermediate elementary reactions included in this pathway with
142 their rate constant. We obtained global rate constants (Equations (E1) and (E2)) by the quasi-steady-
143 state assumption (QSSA):

144 $k_{R11,d} = 1200 T^{0.072} \exp\left(-\frac{27600}{RT}\right)$ (E1)

145 $k_{R11,r} = 6910 T^{-1.863} \exp\left(\frac{4250}{RT}\right)$ (E2)

146 with direct constant $k_{R11,d}$ and reverse constant $k_{R11,r}$ in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, temperature T in K and gas
147 constant R in $\text{cal mol}^{-1} \text{K}^{-1}$. This pathway is sensitive on indene amount, especially reaction (-R10)
148 producing benzyl: the addition of benzyl radical on acetylene also produces indene via an intermediate
149 radical ($C_6H_5-CH_2-CH=CH$). About 70% of benzyl comes from reaction (-R10). Similarly to
150 cyclopentadiene, indene is an important intermediate in PAH growth. It is a precursor of heavy
151 compounds as, for example, cyclopentadiene produces naphthalene [16].

152

153 2.3. Formation of PAHs

154 Among the sixteen EPA-PAHs, six which include two to four rings were already present in the
155 model: naphthalene, acenaphthylene, phenanthrene, anthracene, pyrene and chrysene. Nine have been
156 added with their formation reactions coming from Norinaga et al.'s model [32]: acenaphthene,
157 fluorene, fluoranthene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene,
158 benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene. The formation and the consumption
159 of these species involve a significant number of other species whose inclusion in the model has been
160 necessary. Among them, there are a lot of radical species and other PAHs like acephenanthrylene,

161 benzo[*e*]pyrene, perylene, anthanthrene or coronene. Eventually, the sixteenth EPA-PAH is
162 dibenzo[*a,h*]anthracene. To our knowledge, there is no model in the literature, which describes
163 pathways leading to it. Reactions have been written based on those producing benzo[*a*]anthracene,
164 with the same kinetic coefficients. Reactions implying dibenzo[*a,h*]anthracene or radicals, which
165 derive from it, are reported in Table 1. Figure 1 shows the species involved with their corresponding
166 notations. Dibenzo[*a,h*]anthracene can be produced via different pathways:

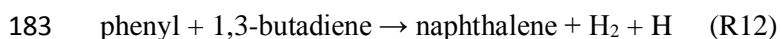
- 167 - from phenanthrene directly, by addition with phenylacetylene or derived radicals (Reactions 1
168 and 2 in Table 1).
- 169 - from benzo[*a*]anthracene, by the HACA mechanism or by addition of derived radicals with
170 vinylacetylene (Reactions 3 to 6).
- 171 - by combination of species with a five-membered ring, such as benzo[*e*]indenyl radical with
172 indenyl radical (Reactions 7 and 8).

173 From this point, missing reaction pathways have been added to improve the simulation of the
174 amount of several PAHs, which were significantly underestimated.

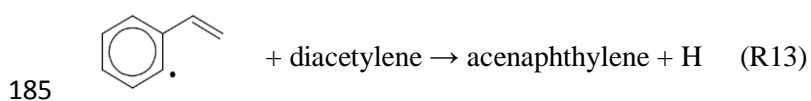
175 In Norinaga et al [32], phenanthrene formation can occur through combination of two benzyl
176 radicals. These reactions have been included in the model. By analogy, pathways to chrysene and
177 benzo[*a*]anthracene formation have been written from the combination of a benzyl radical with a 1-
178 naphthylmethyl radical for chrysene and a 2-naphthylmethyl radical for benzo[*a*]anthracene. These
179 new pathways are presented in Supplementary data (S4) in the case of benzo[*a*]anthracene formation.

180 Other reactions from the literature have been integrated in order to complete the possible
181 reaction pathways of the following PAHs:

- 182 - naphthalene [24]:



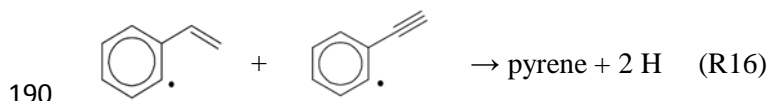
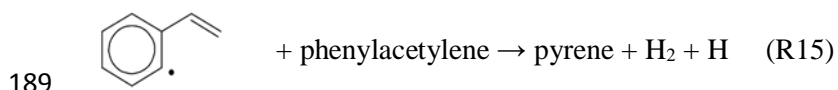
- 184 - acenaphthylene [17]:



- 186 - chrysene [32]:

187 indenyl + indenyl \rightarrow chrysene + 2 H (R14)

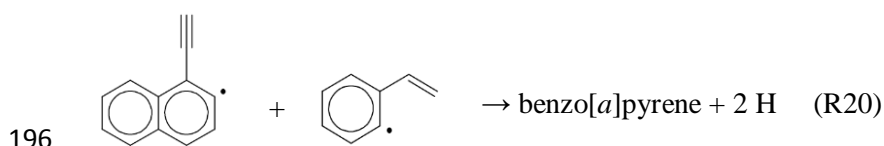
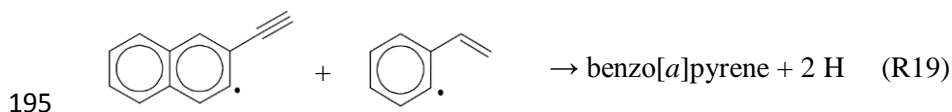
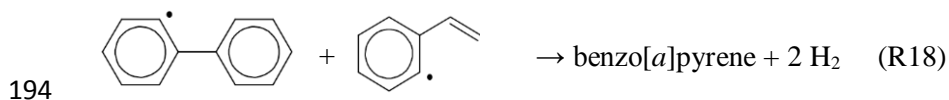
188 - pyrene [24]:



191 - benzo[ghi]fluoranthene [17]:

192 indenyl + indenyl \rightarrow benzo[ghi]fluoranthene + 2 H₂ (R17)

193 - benzo[a]pyrene [24]:



197 Note that these reactions are not elementary steps but a lumping of successive reactions, and are
198 therefore irreversible.

199

200 2.4. Influence of acetone

201 Because of the presence of acetone in acetylene bottles to avoid self-detonation, five reactions
202 of the decomposition of acetone have been included in the mechanism. They come from the model of
203 Norinaga and Deutschmann [31]. Despite the low amount of this impurity, acetone is very reactive and
204 it dominates radical initiation during acetylene pyrolysis in our operating conditions, especially by
205 methyl radical formation [58].

206

207 **3. Model validation**

208 The validation of the model was realized thanks to various experimental data available in the
209 literature. In this section, the simulations were obtained in the operating conditions of Norinaga and
210 Deutschmann [31] at low pressure and in those of Sánchez et al. [38,39] at atmospheric pressure for
211 acetylene and ethylene pyrolysis in a plug-flow reactor. Simulations were performed using the PSR
212 (Perfectly Stirred Reactor model) module in the Chemkin software suite. The plug-flow reactor was
213 modeled as a succession of continuous stirred-tank reactors. A series of fifty PSRs were used in order
214 to obtain solutions independent of the number of elementary reactors. Error factors in section 3.1 have
215 been calculated for the experimental point available at the longest residence time.

216

217 **3.1. Low-pressure pyrolysis - Comparison with Norinaga and Deutschmann results**

218 *3.1.1. Acetylene pyrolysis*

219 The inlet stream of the reactor is composed of 98% acetylene, 0.2% methane and 1.8%
220 acetone. Figures 2, 3 and 4 compare simulations with experimental points [31]. Simulations in the
221 same conditions with the model of Norinaga et al. [32] are also represented. Graphs present the
222 evolution of mole fractions of the different species plotted as a function of the residence time into the
223 reactor. Figure 2 shows results for light species, i.e. the consumption of acetylene and the formation of
224 hydrogen, methane, ethylene, vinylacetylene and propyne, at 1173 K and 8 kPa. Figure 3 shows the
225 profiles of benzene, toluene, styrene, indene, naphthalene and acenaphthylene at 1173 K and 8 kPa.
226 Eventually, the formation of heavier PAHs at 1173 K and 15 kPa is presented in Figure 4. Some EPA-
227 PAHs were not quantified experimentally. They are treated in section 3.2. Regarding experiments,
228 material balances show that more than 90% carbon is generally analyzed at the outlet [42]. The
229 estimated uncertainties for concentrations range between $\pm 9\%$ and $\pm 32\%$, increasing with the
230 molecular weight of molecules [31].

231 Simulation agrees with experimental points for acetylene, vinylacetylene and propyne.
232 Hydrogen and methane are underestimated (by a factor 1.8) and ethylene is overestimated (by a factor
233 3). Regarding first aromatic rings, benzene and styrene, which are the major aromatic species
234 quantified experimentally, are fairly well represented by the model. The main primary product of

235 acetylene pyrolysis is vinylacetylene, which mostly leads to benzene and styrene formation. For these
236 compounds, our simulations better represent experimental points than the model of Norinaga et al.
237 (especially for vinylacetylene). Meanwhile, ethylene is overpredicted. Flux analysis, detailed in
238 Supplementary data (S5), shows that it is produced from vinylacetylene by decomposition into vinyl
239 radical, which leads to ethylene, but also by decomposition of phenylethyl radical, which comes from
240 styrene. Styrene is mainly produced from benzene. In the model, added reactions of vinylacetylene
241 lead to the formation of benzene and styrene (reactions (R2) to (R8)), and so, to the formation of
242 ethylene. In this way, the overprediction of ethylene is related to the much better representation of
243 vinylacetylene compared to Norinaga's model, but ethylene plays a less important role in aromatic
244 formation [31]. Therefore, the first steps of the pyrolysis are correctly described by the model.
245 Tendencies of toluene and indene are not well represented. They reach a maximum for a short
246 residence time while experimental points present a monotonic growth on the range of studied
247 residence times. These two species are correlated by reaction (R11), discussed in section 2.2.

248 In a general way, simulation reproduces well the order of magnitude of PAH mole fractions.
249 Compared to the model of Norinaga et al., our model gives results closer to experimental data for most
250 PAHs. Some compounds like naphthalene, acenaphthylene and benzo[*k*]fluoranthene are fairly well
251 represented. However, some other profiles have a convex shape while experimental curves have a
252 concave shape. Phenanthrene is overestimated (by a factor 2.4) while anthracene is underestimated (by
253 a factor 3). These two species are linked in the model: higher amounts of anthracene leads to higher
254 amounts of phenanthrene and vice versa. Flux analysis shows that the main pathway for anthracene
255 formation is the isomerization of phenanthrene, which is also the most sensitive reaction on anthracene
256 formation. However, increasing the kinetic constant of this reversible reaction (which comes from
257 Marinov et al. [59]) by a factor 10 has almost no effect on concentration, whereas the sensitivity
258 coefficient of the reaction drops off. The equilibrium constant of the reaction of isomerization is then
259 more sensitive: decreasing the enthalpy of formation of anthracene by 4 kcal mol⁻¹ permits to fit the
260 mole fraction of this species in acetylene pyrolysis conditions. However, the enthalpy of formation
261 used in the model for anthracene and phenanthrene are from Kudchadker et al. [60], i.e. 55.0 kcal mol⁻¹
262 and 49.5 kcal mol⁻¹, respectively. These data are in very good agreement with the review of Roux et al.

263 [61] (54.8 ± 0.7 kcal mol⁻¹ and 48.3 ± 0.6 kcal mol⁻¹ respectively). A larger spread between enthalpies of
264 formation of both isomers would be far beyond the range of uncertainty. Note that the main pathway
265 for phenanthrene formation is the addition of a radical derived from phenylacetylene on benzene. This
266 pathway cannot lead to the formation of anthracene but another important pathway for anthracene
267 formation can be missing. Benzo[ghi]perylene is significantly underestimated (by a factor 21), even if
268 its mole fraction is the lowest among quantified PAHs. Some formation pathways should still be
269 missing. It is produced by the HACA mechanism from benzo[e]pyrene and perylene and consumed to
270 produce coronene. Another pathway could be the addition of aromatic rings on lighter PAHs such as
271 phenanthrene.

272

273 3.1.2. Ethylene pyrolysis

274 The inlet stream of the reactor is composed of 99.4% ethylene, 0.2% methane and 0.4%
275 ethane. Figures 5 and 6 show the evolution of mole fractions of light species and of first aromatic rings
276 and light PAHs respectively, plotted as a function of the residence time, at 1173 K and 8 kPa. Figure 7
277 shows profiles of heavy EPA-PAHs for which experimental points [31] exist at 1173 K and 15 kPa. As
278 in the case of acetylene pyrolysis, simulations with the model of Norinaga et al. [32] are presented for
279 comparison.

280 Ethylene consumption is well represented by the model as well as hydrogen, acetylene and
281 vinylacetylene profiles overall. Methane production is underestimated (by a factor 1.8) and 1,3-
282 butadiene is overestimated (by a factor 2) although the curve correctly represents its tendency.
283 Regarding first aromatic rings, the model well describes benzene evolution. Profiles are fairly well
284 respected so it is possible to consider that the model correctly represents the first steps of ethylene
285 pyrolysis despite differences observed for toluene and styrene as well as for indene from some
286 residence time (compounds in much smaller amounts than benzene). The link between toluene and
287 indene was mentioned in section 3.1.1. The validation of the model for the formation of light species is
288 confirmed by the good agreement of simulation results with experimental data for light PAHs, namely
289 naphthalene, acenaphthylene and phenanthrene. Anthracene is underestimated (by a factor 13).

290 Generally, tendencies and orders of magnitude of heavier PAHs are fairly well represented.
291 However, the model underestimates pyrene formation (by a factor 8.2) and overestimates chrysene and
292 benzo[*a*]anthracene formation (by a factor 1.8 and 2.4 respectively). A flux analysis shows that the
293 main reaction pathways of formation of these four-ring compounds differ between ethylene pyrolysis
294 and acetylene pyrolysis. In the case of ethylene, chrysene and benzo[*a*]anthracene are mainly produced
295 (at 91% and 87% respectively for a residence time of 1 s) by combination of two indenyl radicals
296 which come from indene. These pathways may be too fast. It could explain chrysene and
297 benzo[*a*]anthracene overestimation along with indene underestimation for large residence times. As to
298 pyrene, the formation pathway by addition of a styryl radical on phenylacetylene which is important
299 during acetylene pyrolysis (46% for a residence time of 1 s) is negligible during ethylene pyrolysis
300 (1.7% for a residence time of 1 s). The underestimation of styrene by the simulation can cause this
301 change. So, improving styrene profile might allow to enhance pyrene formation. Otherwise, the model
302 reproduces benzo[*a*]pyrene evolution very well but it underestimates fluoranthene and
303 benzo[*k*]fluoranthene formation (by a factor 12 and 14, respectively).

304 Our simulations give much better results than those of Norinaga et al. for benzene, light PAHs
305 (naphthalene, acenaphthylene and phenanthrene) and benzo[*a*]pyrene but they are worse for some
306 heavier PAHs. Nevertheless, naphthalene, which experimental fraction is up to 100 times higher than
307 that of other PAHs, is very well predicted here, while Norinaga's model overestimates it by a factor of
308 4. Since naphthalene is one of the base compounds in PAH enlargement, this explain partly the present
309 fluoranthene and benzo[*k*]fluoranthene underestimation. A flux analysis shows that fluoranthene
310 mainly comes (at 67% for a residence time of 1 s) from the addition of a phenyl radical on naphthalene
311 or of a naphthyl radical on benzene. As to benzo[*k*]fluoranthene, it is formed by the addition of a
312 naphthyl radical on naphthalene.

313

314 3.2. Atmospheric pyrolysis - Comparison with Sánchez et al. results

315 Sánchez et al. quantified the sixteen EPA-PAHs during acetylene and ethylene pyrolysis under
316 various conditions of temperature [38,39,41], residence time [41] and concentration [39]. They worked
317 at atmospheric pressure, leading to soot formation despite the low fraction of hydrocarbon (3%)

318 diluted in nitrogen. It makes the comparison with the model difficult because the model does not
319 include soot formation. Moreover, pressure changes kinetics of some reactions.

320 Simulations were realized at 1173 K and atmospheric pressure for a residence time of 1.45 s.
321 The inlet stream of the reactor is composed of 3% reactant (acetylene or ethylene) and 97% inert
322 (nitrogen), which corresponds to a partial pressure of 3 kPa for the reactant. Temperature of 1173 K
323 has been chosen to make easier the comparison with experimental data: at a lower temperature, too
324 few PAHs are formed and at a higher temperature, soot formation becomes important.

325 Absolute simulated amounts of each PAH are much lower than experimental results except for
326 naphthalene during ethylene pyrolysis. The authors give a carbon yield of light compounds (from H₂ to
327 C₈) [38,39] and it seems that the model overestimates these light compounds while it underestimates
328 PAHs. In particular, available data on benzene during acetylene pyrolysis [39] show that this
329 compound is overestimated in simulations. All of this suggests that PAH formation from light species
330 and first aromatic rings is too slow in these conditions and that the influence of the pressure is not well
331 taken into account in the model. Nevertheless, without more detailed experimental data on light
332 compounds, it is not possible to make conclusive hypotheses. A quantitative comparison between
333 experiments and simulations results cannot be performed. Following observations are qualitative.

334 In both experiments and simulations, acetylene pyrolysis produces larger amounts of all PAHs
335 than ethylene pyrolysis, except for acenaphthene. In a general way, predicted relative amounts of
336 PAHs, compared one to another, agree with experiments. Experimentally, the predominant PAHs are
337 the lightest up to pyrene except for acenaphthene, which is formed in small amount. This result is
338 found by simulation but with some differences. On one hand, anthracene is predicted in too small
339 amount. On the other hand, in ethylene pyrolysis, benzo[*a*]anthracene and chrysene are predicted in
340 larger amounts than pyrene. These elements are consistent with the observations made at low pressure
341 and discussed in section 3.1.

342 About PAHs which were not quantified by Norinaga et al., simulations seem to lead to correct
343 orders of magnitude for fluorene, benzo[*b*]fluoranthene and dibenzo[*a,h*]anthracene compared to other
344 PAHs. Acenaphthene is predicted in too small amount during acetylene pyrolysis but is well
345 represented during ethylene pyrolysis. It can be explain by the fact that acenaphthene is

346 overwhelmingly produced in the model by the addition of an 1-naphthyl radical on ethylene.
347 Alternative pathways may take place during acetylene pyrolysis. This makes consistent the
348 predominance of acenaphthene during ethylene pyrolysis at 1173 K, i.e. at lower temperature than
349 what is experimentally observed. Indeno[1,2,3-*cd*]pyrene seems underestimated compared to other
350 PAHs. Some formation pathways for this compound must be missing in the model. For now, it is only
351 produced from pyrene by addition of benzene or phenyl and from benzo[*b*]fluoranthene by the HACA
352 mechanism. Benzo[*ghi*]perylene seems also underestimated during ethylene pyrolysis as during
353 acetylene pyrolysis. Its formation pathways were already discussed in section 3.1.1.

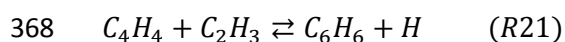
354

355 **4. Discussion**

356 **4.1. Reaction pathways of benzene production**

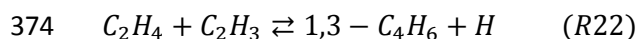
357 It is essential to predict accurately benzene evolution because it is one of the main precursors
358 of PAHs. Moreover, it plays a major role in their growth thanks to the combinative growth
359 mechanism. In section 1, the main pathways of formation of benzene described in the literature were
360 recalled, but the model takes into account many other pathways. A flux analysis was realized in order
361 to determine the origin of benzene in the case of pyrolysis of different hydrocarbons. Simulations were
362 performed at 1173 K, 8 kPa and a reactant conversion of approximately 40%. This conversion
363 corresponds to a residence time of 1 s for acetylene and ethylene, a residence time of 0.22 s for
364 propylene and a residence time of 0.003 s for propane. In each case, reactant is considered pure. Figure
365 8 details the main pathways of the formation of benzene during acetylene and ethylene pyrolysis.

366 Regarding acetylene pyrolysis, benzene mainly comes from the addition reaction of
367 vinylacetylene with acetylene molecules (R2) or with vinyl radicals (R21):

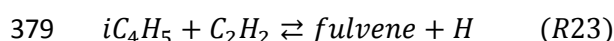


369 Vinylacetylene is largely formed by addition of two acetylene molecules, either directly (R1) or via
370 diacetylene and iC_4H_3 radical ($HC \equiv C - C = CH_2$).

371 During ethylene pyrolysis, two major reaction pathways, which are roughly equivalent,
372 appear. Both involve 1,3-butadiene, one of the major product, mainly formed by the addition of vinyl
373 radical on an ethylene molecule:



375 The first pathway is the cyclization of a linear C_6H_9 radical ($CH_2=CH-CH_2-CH=CH-CH_2$), which is
376 produced by the addition of vinyl radical on 1,3-butadiene. The second involves fulvene, which
377 undergoes an isomerization to benzene. Fulvene is mainly formed from iC_4H_5 radical ($H_2C=CH-$
378 $C=CH_2$) by the following reaction:



380 iC_4H_5 radical is produced by H-atom abstractions on 1,3-butadiene.

381 Lastly, the model was used to simulate propylene pyrolysis and propane pyrolysis. Reaction
382 pathways to benzene are similar in both cases. Benzene comes mainly from fulvene isomerization.
383 However, unlike ethylene pyrolysis, fulvene is formed from propylene thanks to a reaction chain
384 involving different C_3 species. These reactions are the following:

- 385 - formation of tC_3H_5 radical ($H_2C=C-CH_3$) from propylene by H-atom abstraction
- 386 - formation of allene by β -scission of tC_3H_5 radical
- 387 - formation of propargyl radical C_3H_3 from allene by H-atom abstraction
- 388 - combination of a propargyl radical with an allyl radical or with another propargyl radical to
389 form fulvene. Allyl radicals are derived from propylene by H-atom abstraction.

390 In the case of propane pyrolysis, H-atom abstraction reactions of propane lead to iC_3H_7 radical (H_3C-
391 $CH-CH_3$), which produces propylene by β -scission.

392 The different reaction pathways to benzene, which have been detailed here, represent the
393 major pathways for the different reactants. Nevertheless, minor pathways involve other cyclic species
394 such as methylcyclopentadiene, toluene, styrene or 1,3,5,7-cyclooctatetraene.

395

396 4.2. Influence of the reactant on the formation of PAHs

397 The model was used to compare PAH formation during the pyrolysis of three different
398 hydrocarbons: acetylene, ethylene and propane. These reactants were chosen because they are the
399 compounds most used in low-pressure gas carburizing [37] and because they represent an alkyne, an
400 alkene and an alkane, respectively.

401 As an order of magnitude, Figure 9 presents mole fractions for each of the sixteen EPA-PAHs
402 produced by the pyrolysis of the three pure reactants at 1173 K, 15 kPa and at a reactant conversion of
403 50%. This conversion is equivalent to a residence time of 0.68 s for acetylene, 1.05 s for ethylene and
404 $3.9 \cdot 10^{-3}$ s for propane. Propane conversion is much faster than acetylene or ethylene conversion
405 because of fast reactions of C-C bond breaking [62]. To better understand the results, a flux analysis
406 for benzo[*a*]pyrene formation is presented in Figure 10. It shows the pathways of formation of
407 benzo[*a*]pyrene during acetylene and ethylene pyrolysis. Propane pyrolysis is not represented on the
408 figure but pathways are similar to those for ethylene: benzo[*a*]pyrene is produced from
409 benzo[*a*]anthracene at 26% and from chrysene at 70% (via intermediate radicals); benzo[*a*]anthracene
410 and chrysene are formed from the recombination of two indenyl radicals at 98% and 99% respectively.
411 Figure 9 shows that all PAHs are present in larger amounts during acetylene pyrolysis than during
412 ethylene pyrolysis, which joins the results of section 3. This is explained by the importance of the
413 HACA mechanism in the process of PAH growth, which can be noticed in Figure 10. Benzo[*a*]pyrene
414 is almost entirely produced through this mechanism from benzo[*a*]anthracene and chrysene. These two
415 PAHs are produced by combination of two indenyl radicals during ethylene pyrolysis but they are
416 mainly produced from naphthyl radicals or naphthalene during acetylene pyrolysis. Pathways for
417 naphthalene formation are presented in Supplementary data (S6). They show that the HACA
418 mechanism is mostly responsible for the production of naphthalene during acetylene pyrolysis.
419 Otherwise, Figure 9 shows that for propane pyrolysis, PAHs are formed in much lower amounts,
420 especially for the heaviest. Alkanes are less favorable to the formation of aromatic rings because C/H
421 ratio is smaller than for alkenes or alkynes. It is therefore necessary to produce unsaturated products to
422 allow cyclisation and aromatic formation. Moreover, because of the weakness of C-C bonds, propane
423 pyrolysis generates many radicals. These radicals have to lead first to the formation of unsaturated
424 molecules (acetylene, ethylene), which then allow PAH formation.

425 However, these results are obtained for the same conversion rate but for different residence
426 times. In industrial gas carburizing, residence time into the reactor is an important parameter because it
427 has an influence on the amount of carbon adsorbed on steel. Figure 11 represents the evolution of the
428 mole fraction of benzo[*a*]pyrene plotted as a function of the residence time for acetylene, ethylene and
429 propane pyrolysis at 1173 K and 15 kPa. On the one hand, benzo[*a*]pyrene is always more produced
430 by acetylene than ethylene. On the other hand, this PAH is more produced by propane than acetylene
431 or ethylene at low residence times because of fast conversion of propane. Propane conversion is
432 stabilized very quickly since it reaches 99% at 0.04 s while acetylene and ethylene conversion
433 gradually increases. From 0.4 s, propane produces less benzo[*a*]pyrene than acetylene (converted at
434 38%) and from 0.98 s, it produces less benzo[*a*]pyrene than ethylene (converted at 49%). Other PAHs
435 have a similar trend. A sensitivity analysis was carried out at a residence time of 1 s and 1173 K to
436 highlight the reactions which impact the production of benzo[*a*]pyrene. It is available in
437 Supplementary data (S7). During acetylene, ethylene and propane pyrolysis, the kinetically limiting
438 reaction for benzo[*a*]pyrene is the addition of a radical derived from benzo[*a*]anthracene on acetylene
439 to form benzo[*a*]pyrene. This strengthens the previous observations on the importance of the HACA
440 mechanism. Other sensitive reactions during acetylene pyrolysis are those of formation and
441 consumption of iC_4H_3 radical, which is an important intermediate of benzene formation (Figure 8).
442 During ethylene and propane pyrolysis, sensitive reactions on benzo[*a*]pyrene involve chrysene and
443 derived radicals, and benzyl radical which is an important intermediate of indene formation
444 (Supplementary data (S6)). Similarities between ethylene and propane are understandable because
445 ethylene is the main primary product of propane pyrolysis.

446 Acetylene produces more PAHs than propane from some residence time but it is also one of
447 the most efficient hydrocarbons for surface reactions [63]. By making the approximation that only
448 acetylene is adsorbed on steel, the time required for carburizing depends on the amount of acetylene
449 available in gas phase, more important for acetylene pyrolysis than for propane pyrolysis. By dividing
450 mole fractions of PAHs for a residence time of 1 s by the mole fraction of acetylene present at this
451 time, several PAHs are formed in larger amount for propane than for acetylene, including
452 benzo[*a*]pyrene. These results are presented in Figure 12 for the sixteen EPA-PAHs.

453

454 **5. Conclusion**

455 A detailed kinetic model has been developed to describe the formation of PAHs from light
456 hydrocarbon pyrolysis (acetylene, ethylene, etc.). It is mainly focused on the formation of the sixteen
457 EPA-PAHs at low pressure. The aim is to use the model to evaluate the potential of toxicity, especially
458 linked to benzo[*a*]pyrene concentration, of processes such as low-pressure gas carburizing. It was
459 validated by various experimental data from the literature. Compared to previous model, it includes
460 new reaction pathways from the literature and represents an improvement for the reactions of small
461 unsaturated species and for the formation of first rings. However, some differences with experimental
462 points are observed, which shows that some reaction pathways are still missing or wrongly evaluated.

463 Simulations allowed to highlight the diversity of reaction pathways leading to benzene and to
464 show the strong dependence between reactant and the predominance of some pathways compared to
465 others. They also allowed to compare PAH formation during the pyrolysis of different hydrocarbons.

466 Experiments of acetylene, ethylene and propane pyrolysis will be performed in the near future
467 in a plug-flow reactor and in a perfectly stirred reactor. They will allow a better validation of the
468 model in low-pressure gas carburizing conditions. Some experiments will be carried out with an iron
469 piece to study the influence of surface reactions on PAH formation and to determine how it is possible
470 to insert those reactions in the model.

471 **Supplementary data**

472 Mechanism **and transport data in CHEMKIN format**, and Supplementary data associated with this
473 article can be found in the online version.

474 **References**

- 475 [1] K. Yada, O. Watanabe, Reactive flow simulation of vacuum carburizing by acetylene gas,
476 *Comput. Fluids*. 79 (2013) 65–76. doi:10.1016/j.compfluid.2013.03.005.
- 477 [2] H. Richter, J.B. Howard, Formation of polycyclic aromatic hydrocarbons and their growth to
478 soot—a review of chemical reaction pathways, *Prog. Energy Combust. Sci.* 26 (2000) 565–608.
- 479 [3] K. Straif, R. Baan, Y. Grosse, B. Secretan, F. El Ghissassi, V. Cogliano, Carcinogenicity of polycyclic
480 aromatic hydrocarbons, *Lancet Oncol.* 6 (2005) 931–932. doi:10.1016/S1470-2045(05)70458-7.
- 481 [4] I. Nisbet, P. Lagoy, Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons
482 (PAHs), *Regul. Toxicol. Pharmacol.* 16 (1992) 290–300. doi:10.1016/0273-2300(92)90009-X.

- 483 [5] C. Champmartin, F. Jeandel, H. Monnier, Maintenance of Low-Pressure Carburizing Furnaces: A
484 Source of PAH Exposure, *Ann. Occup. Hyg.* (2016).
- 485 [6] N.E. Sánchez, A. Callejas, J. Salafranca, Á. Millera, R. Bilbao, M.U. Alzueta, Formation and
486 characterization of polyaromatic hydrocarbons, in: *Clean. Combust. - Dev. Detail. Chem. Kinet.*
487 *Models*, 2013: pp. 283–302.
- 488 [7] H. Wang, M. Frenklach, A detailed kinetic modeling study of aromatics formation in laminar
489 premixed acetylene and ethylene flames, *Combust. Flame.* 110 (1997) 173–221.
- 490 [8] H.A. Gueniche, J. Biet, P.A. Glaude, R. Fournet, F. Battin-Leclerc, A comparative study of the
491 formation of aromatics in rich methane flames doped by unsaturated compounds, *Fuel.* 88
492 (2009) 1388–1393. doi:10.1016/j.fuel.2009.03.006.
- 493 [9] P.R. Westmoreland, A.M. Dean, J.B. Howard, J.P. Longwell, Forming benzene in flames by
494 chemically activated isomerization, *J. Phys. Chem.* 93 (1989) 8171–8180.
495 doi:10.1021/j100362a008.
- 496 [10] J.A. Miller, C.F. Melius, Kinetic and thermodynamic issues in the formation of aromatic
497 compounds in flames of aliphatic fuels, *Combust. Flame.* 91 (1992) 21–39. doi:10.1016/0010-
498 2180(92)90124-8.
- 499 [11] J.A. Miller, S.J. Klippenstein, The Recombination of Propargyl Radicals and Other Reactions on a
500 C₆H₆ Potential, *J. Phys. Chem. A.* 107 (2003) 7783–7799. doi:10.1021/jp030375h.
- 501 [12] R.X. Fernandes, H. Hippler, M. Olzmann, Determination of the rate coefficient for the C₃H₃ +
502 C₃H₃ reaction at high temperatures by shock-tube investigations, *Proc. Combust. Inst.* 30
503 (2005) 1033–1038. doi:10.1016/j.proci.2004.08.204.
- 504 [13] C.F. Melius, M.E. Colvin, N.M. Marinov, W.J. Pitz, S.M. Senkan, Reaction mechanisms in
505 aromatic hydrocarbon formation involving the C₅H₅ cyclopentadienyl moiety, *Symp. Int.*
506 *Combust.* 26 (1996) 685–692. doi:10.1016/S0082-0784(96)80276-1.
- 507 [14] A.M. Mebel, V.V. Kislov, Can the C₅H₅ + C₅H₅ → C₁₀H₁₀ → C₁₀H₉ + H/C₁₀H₈ + H₂ Reaction
508 Produce Naphthalene? An Ab Initio/RRKM Study, *J. Phys. Chem. A.* 113 (2009) 9825–9833.
509 doi:10.1021/jp905931j.
- 510 [15] C. Cavallotti, D. Polino, On the kinetics of the C₅H₅ + C₅H₅ reaction, *Proc. Combust. Inst.* 34
511 (2013) 557–564. doi:10.1016/j.proci.2012.05.097.
- 512 [16] N.M. Marinov, W.J. Pitz, C.K. Westbrook, A.M. Vincitore, M.J. Castaldi, S.M. Senkan, C.F. Melius,
513 Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Laminar Premixed n-Butane
514 Flame, *Combust. Flame.* 114 (1998) 192–213. doi:10.1016/S0010-2180(97)00275-7.
- 515 [17] N.A. Slavinskaya, P. Frank, A modelling study of aromatic soot precursors formation in laminar
516 methane and ethene flames, *Combust. Flame.* 156 (2009) 1705–1722.
517 doi:10.1016/j.combustflame.2009.04.013.
- 518 [18] M. Frenklach, D.W. Clary, W.C. Gardiner Jr., S.E. Stein, Detailed kinetic modeling of soot
519 formation in shock-tube pyrolysis of acetylene, *Symp. Int. Combust.* 20 (1984) 887–901.
520 doi:10.1016/S0082-0784(85)80578-6.
- 521 [19] V.V. Kislov, A.I. Sadovnikov, A.M. Mebel, Formation Mechanism of Polycyclic Aromatic
522 Hydrocarbons beyond the Second Aromatic Ring, *J. Phys. Chem. A.* 117 (2013) 4794–4816.
523 doi:10.1021/jp402481y.
- 524 [20] H. Böhm, H. Jander, PAH formation in acetylene–benzene pyrolysis, *Phys. Chem. Chem. Phys.* 1
525 (1999) 3775–3781.
- 526 [21] B. Shukla, M. Koshi, A novel route for PAH growth in HACA based mechanisms, *Combust. Flame.*
527 159 (2012) 3589–3596. doi:10.1016/j.combustflame.2012.08.007.
- 528 [22] V.V. Kislov, N.I. Islamova, A.M. Kolker, S.H. Lin, A.M. Mebel, Hydrogen Abstraction Acetylene
529 Addition and Diels–Alder Mechanisms of PAH Formation: A Detailed Study Using First Principles
530 Calculations, *J. Chem. Theory Comput.* 1 (2005) 908–924. doi:10.1021/ct0500491.
- 531 [23] J. Appel, H. Bockhorn, M. Frenklach, Kinetic modeling of soot formation with detailed chemistry
532 and physics: laminar premixed flames of C₂ hydrocarbons, *Combust. Flame.* 121 (2000) 122–
533 136. doi:10.1016/S0010-2180(99)00135-2.

- 534 [24] V. Chernov, M.J. Thomson, S.B. Dworkin, N.A. Slavinskaya, U. Riedel, Soot formation with C1
535 and C2 fuels using an improved chemical mechanism for PAH growth, *Combust. Flame*. 161
536 (2014) 592–601. doi:10.1016/j.combustflame.2013.09.017.
- 537 [25] C. Saggese, N.E. Sánchez, A. Frassoldati, A. Cuoci, T. Faravelli, M.U. Alzueta, E. Ranzi, Kinetic
538 Modeling Study of Polycyclic Aromatic Hydrocarbons and Soot Formation in Acetylene Pyrolysis,
539 *Energy Fuels*. 28 (2014) 1489–1501. doi:10.1021/ef402048q.
- 540 [26] K. Wang, S.M. Villano, A.M. Dean, Fundamentally-based kinetic model for propene pyrolysis,
541 *Combust. Flame*. 162 (2015) 4456–4470. doi:10.1016/j.combustflame.2015.08.012.
- 542 [27] C. Xu, A.S. Al Shoaibi, C. Wang, H.-H. Carstensen, A.M. Dean, Kinetic Modeling of Ethane
543 Pyrolysis at High Conversion, *J. Phys. Chem. A*. 115 (2011) 10470–10490.
544 doi:10.1021/jp206503d.
- 545 [28] I. Ziegler, R. Fournet, P.M. Marquaire, Pyrolysis of propane for CVI of pyrocarbon: Part I.
546 Experimental and modeling study of the formation of toluene and aliphatic species, *J. Anal.*
547 *Appl. Pyrolysis*. 73 (2005) 212–230. doi:10.1016/j.jaap.2004.12.005.
- 548 [29] I. Ziegler, R. Fournet, P.-M. Marquaire, Pyrolysis of propane for CVI of pyrocarbon: Part II.
549 Experimental and modeling study of polyaromatic species, *J. Anal. Appl. Pyrolysis*. 73 (2005)
550 231–247. doi:10.1016/j.jaap.2005.03.007.
- 551 [30] K. Norinaga, O. Deutschmann, *Proc. EUROCVI-15*, (2005). <http://www.detchem.com/> (accessed
552 June 24, 2014).
- 553 [31] K. Norinaga, O. Deutschmann, Detailed kinetic modeling of gas-phase reactions in the chemical
554 vapor deposition of carbon from light hydrocarbons, *Ind. Eng. Chem. Res*. 46 (2007) 3547–3557.
- 555 [32] K. Norinaga, O. Deutschmann, N. Saegusa, J. Hayashi, Analysis of pyrolysis products from light
556 hydrocarbons and kinetic modeling for growth of polycyclic aromatic hydrocarbons with
557 detailed chemistry, *J. Anal. Appl. Pyrolysis*. 86 (2009) 148–160. doi:10.1016/j.jaap.2009.05.001.
- 558 [33] R.U. Khan, S. Bajohr, D. Buchholz, R. Reimert, H.D. Minh, K. Norinaga, V.M. Janardhanan, S.
559 Tischer, O. Deutschmann, Pyrolysis of propane under vacuum carburizing conditions: An
560 experimental and modeling study, *J. Anal. Appl. Pyrolysis*. 81 (2008) 148–156.
561 doi:10.1016/j.jaap.2007.09.012.
- 562 [34] A. Matsugi, A. Miyoshi, Modeling of two- and three-ring aromatics formation in the pyrolysis of
563 toluene, *Proc. Combust. Inst*. 34 (2013) 269–277. doi:10.1016/j.proci.2012.06.032.
- 564 [35] B. Shukla, A. Susa, A. Miyoshi, M. Koshi, In Situ Direct Sampling Mass Spectrometric Study on
565 Formation of Polycyclic Aromatic Hydrocarbons in Toluene Pyrolysis, *J. Phys. Chem. A*. 111
566 (2007) 8308–8324. doi:10.1021/jp071813d.
- 567 [36] B. Shukla, A. Susa, A. Miyoshi, M. Koshi, Role of Phenyl Radicals in the Growth of Polycyclic
568 Aromatic Hydrocarbons, *J. Phys. Chem. A*. 112 (2008) 2362–2369. doi:10.1021/jp7098398.
- 569 [37] D. Buchholz, R.U. Khan, S. Bajohr, R. Reimert, Computational Fluid Dynamics Modeling of
570 Acetylene Pyrolysis for Vacuum Carburizing of Steel, *Ind. Eng. Chem. Res*. 49 (2010) 1130–1137.
571 doi:10.1021/ie900996h.
- 572 [38] N.E. Sánchez, A. Callejas, Á. Millera, R. Bilbao, M.U. Alzueta, Polycyclic Aromatic Hydrocarbon
573 (PAH) and Soot Formation in the Pyrolysis of Acetylene and Ethylene: Effect of the Reaction
574 Temperature, *Energy Fuels*. 26 (2012) 4823–4829. doi:10.1021/ef300749q.
- 575 [39] N.E. Sánchez, Á. Millera, R. Bilbao, M.U. Alzueta, Polycyclic aromatic hydrocarbons (PAH), soot
576 and light gases formed in the pyrolysis of acetylene at different temperatures: Effect of fuel
577 concentration, *J. Anal. Appl. Pyrolysis*. 103 (2013) 126–133. doi:10.1016/j.jaap.2012.10.027.
- 578 [40] N.E. Sánchez, J. Salafranca, A. Callejas, Á. Millera, R. Bilbao, M.U. Alzueta, Quantification of
579 polycyclic aromatic hydrocarbons (PAHs) found in gas and particle phases from pyrolytic
580 processes using gas chromatography–mass spectrometry (GC–MS), *Fuel*. 107 (2013) 246–253.
581 doi:10.1016/j.fuel.2013.01.065.
- 582 [41] N.E. Sánchez, A. Callejas, A. Millera, R. Bilbao, M.U. Alzueta, Formation of PAH and soot during
583 acetylene pyrolysis at different gas residence times and reaction temperatures, *Energy*. 43
584 (2012) 30–36. doi:10.1016/j.energy.2011.12.009.

- 585 [42] K. Norinaga, O. Deutschmann, K.J. Hüttinger, Analysis of gas phase compounds in chemical
586 vapor deposition of carbon from light hydrocarbons, *Carbon*. 44 (2006) 1790–1800.
587 doi:10.1016/j.carbon.2005.12.050.
- 588 [43] B. Husson, M. Ferrari, O. Herbinet, S.S. Ahmed, P.-A. Glaude, F. Battin-Leclerc, New
589 experimental evidence and modeling study of the ethylbenzene oxidation, *Proc. Combust. Inst.*
590 34 (2013) 325–333. doi:10.1016/j.proci.2012.06.002.
- 591 [44] M. Nowakowska, O. Herbinet, A. Dufour, P.-A. Glaude, Detailed kinetic study of anisole pyrolysis
592 and oxidation to understand tar formation during biomass combustion and gasification,
593 *Combust. Flame*. 161 (2014) 1474–1488. doi:10.1016/j.combustflame.2013.11.024.
- 594 [45] H.A. Gueniche, P.A. Glaude, R. Fournet, F. Battin-Leclerc, Rich premixed laminar methane
595 flames doped by light unsaturated hydrocarbons: II. 1,3-Butadiene, *Combust. Flame*. 151 (2007)
596 245–261. doi:10.1016/j.combustflame.2007.05.007.
- 597 [46] H.A. Gueniche, P.A. Glaude, G. Dayma, R. Fournet, F. Battin-Leclerc, Rich methane premixed
598 laminar flames doped with light unsaturated hydrocarbons: I. Allene and propyne, *Combust.*
599 *Flame*. 146 (2006) 620–634. doi:10.1016/j.combustflame.2006.07.004.
- 600 [47] H.A. Gueniche, P.A. Glaude, R. Fournet, F. Battin-Leclerc, Rich methane premixed laminar
601 flames doped by light unsaturated hydrocarbons: III. Cyclopentene, *Combust. Flame*. 152 (2008)
602 245–261. doi:10.1016/j.combustflame.2007.07.012.
- 603 [48] N.A. Slavinskaya, U. Riedel, S.B. Dworkin, M.J. Thomson, Detailed numerical modeling of PAH
604 formation and growth in non-premixed ethylene and ethane flames, *Combust. Flame*. 159
605 (2012) 979–995. doi:10.1016/j.combustflame.2011.10.005.
- 606 [49] C. Muller, V. Michel, G. Scacchi, G. Côme, Thergas - a Computer-Program for the Evaluation of
607 Thermochemical Data of molecules and free-radicals in the gas phase, *J. Chim. Phys. Phys.-*
608 *Chim. Biol.* 92 (1995) 1154–1178.
- 609 [50] O.A. Rokstad, O.A. Lindvaag, A. Holmen, Acetylene Pyrolysis in Tubular Reactor, *Int. J. Chem.*
610 *Kinet.* 46 (2014) 104–115. doi:10.1002/kin.20830.
- 611 [51] D. Dudek, K. Glänzer, J. Troe, Pyrolysis of 1.3.5.7-Cyclooctatetraene, Semibullvalene, and 1.5-
612 Dihydropentalene in Shock Waves and in a Flow System (Part I), *Berichte Bunsen-Ges.-Phys.*
613 *Chem. Chem. Phys.* 83 (1979) 776–788.
- 614 [52] H.J. Curran, Rate constant estimation for C1 to C4 alkyl and alkoxy radical decomposition, *Int. J.*
615 *Chem. Kinet.* 38 (2006) 250–275. doi:10.1002/kin.20153.
- 616 [53] C. Cavallotti, S. Fascella, R. Rota, S. Carrà, A Quantum Chemistry Study of the Formation of Pah
617 and Soot Precursors Through Butadiene Reactions, *Combust. Sci. Technol.* 176 (2004) 705–720.
618 doi:10.1080/00102200490428026.
- 619 [54] V.D. Knyazev, I.R. Slagle, Kinetics of the Reaction between Propargyl Radical and Acetylene, *J.*
620 *Phys. Chem. A*. 106 (2002) 5613–5617. doi:10.1021/jp0144909.
- 621 [55] C. Cavallotti, S. Mancarella, R. Rota, S. Carra, Conversion of C5 into C6 cyclic species through the
622 formation of C7 intermediates, *J. Phys. Chem. A*. 111 (2007) 3959–3969.
623 doi:10.1021/jp067117f.
- 624 [56] J.D. Savee, T.M. Selby, O. Welz, C.A. Taatjes, D.L. Osborn, Time- and Isomer-Resolved
625 Measurements of Sequential Addition of Acetylene to the Propargyl Radical, *J. Phys. Chem. Lett.*
626 6 (2015) 4153–4158. doi:10.1021/acs.jpcllett.5b01896.
- 627 [57] V.V. Kislov, A.M. Mebel, Ab Initio G3-type/Statistical Theory Study of the Formation of Indene in
628 Combustion Flames. I. Pathways Involving Benzene and Phenyl Radical, *J. Phys. Chem. A*. 111
629 (2007) 3922–3931. doi:10.1021/jp067135x.
- 630 [58] M.B. Colket III, D.J. Seery, H.B. Palmer, The pyrolysis of acetylene initiated by acetone,
631 *Combust. Flame*. 75 (1989) 343–366. doi:10.1016/0010-2180(89)90048-5.
- 632 [59] N.M. Marinov, W.J. Pitz, C.K. Westbrook, M.J. Castaldi, S.M. Senkan, Modeling of Aromatic and
633 Polycyclic Aromatic Hydrocarbon Formation in Premixed Methane and Ethane Flames,
634 *Combust. Sci. Technol.* 116–117 (1996) 211–287. doi:10.1080/00102209608935550.

- 635 [60] S.A. Kudchadker, A.P. Kudchadker, B.J. Zwolinski, Chemical thermodynamic properties of
636 anthracene and phenanthrene, *J. Chem. Thermodyn.* 11 (1979) 1051–1059. doi:10.1016/0021-
637 9614(79)90135-6.
- 638 [61] M.V. Roux, M. Temprado, J.S. Chickos, Y. Nagano, Critically Evaluated Thermochemical
639 Properties of Polycyclic Aromatic Hydrocarbons, *J. Phys. Chem. Ref. Data.* 37 (2008) 1855–1996.
640 doi:10.1063/1.2955570.
- 641 [62] Y.-R. Luo, *Handbook of Bond Dissociation Energies in Organic Compounds*, CRC Press, 2003.
- 642 [63] R. Lacroix, R. Fournet, I. Ziegler-Devin, P.-M. Marquaire, Kinetic modeling of surface reactions
643 involved in CVI of pyrocarbon obtained by propane pyrolysis, *Carbon.* 48 (2010) 132–144.
644 doi:10.1016/j.carbon.2009.08.041.

Table

Table 1: Reactions of production and consumption of dibenzo[*a,h*]anthracene (DBAHA3L) and derived radicals with kinetic constants¹ by analogy with benzo[*a*]anthracene reactions

No.	Reaction ²	A (cm ³ mol ⁻¹ s ⁻¹)	n	Ea (cal mol ⁻¹)
1	<i>phenanthrene</i> + C ₆ H ₄ #C ₂ H • ↔ DBAHA3L + H	8.51 10 ¹¹	0	3 987
2	<i>phenanthrene</i> - 2 + C ₆ H ₅ #C ₂ H ↔ DBAHA3L + H	8.51 10 ¹¹	0	3 987
3	BAA3L - 9 + C ₄ H ₄ ↔ DBAHA3L + H	9.90 10 ³⁰	5.07	21 101
4	BAA3L - 8 + C ₄ H ₄ ↔ DBAHA3L + H	9.90 10 ³⁰	5.07	21 101
5	BAA3LE - 1P + C ₂ H ₂ ↔ DBAHA3L - 1	1.87 10 ⁷	1.787	3 262
6	BAA3LE - 2S + C ₂ H ₂ ↔ DBAHA3L - 12	1.87 10 ⁷	1.787	3 262
7	BEindene • +inderyl → DBAHA3L + H + H	1.00 10 ¹²	0	7 999
8	NFindene • +C ₅ H ₅ → DBAHA3L + H + H	1.00 10 ¹²	0	7 999
9	DBAHA3L + H ↔ DBAHA3L - 1 + H ₂	3.23 10 ⁷	2.095	15 843
10	DBAHA3L + H ↔ DBAHA3L - 12 + H ₂	3.23 10 ⁷	2.095	15 843
11	DBAHA3L + H ↔ DBAHA3L - 4 + H ₂	3.23 10 ⁹	2.095	15 843
12	DBAHA3L - 1 + H ↔ DBAHA3L	5.00 10 ¹³	0	0
13	DBAHA3L - 12 + H ↔ DBAHA3L	5.00 10 ¹³	0	0
14	DBAHA3L - 4 + H ↔ DBAHA3L	5.00 10 ¹³	0	0
15	DBAHA3L + CH ₃ ↔ DBAHA3L - 1 + CH ₄	2.00 10 ¹²	0	15 059
16	DBAHA3L + CH ₃ ↔ DBAHA3L - 12 + CH ₄	2.00 10 ¹²	0	15 059
17	DBAHA3L + C ₂ H ₃ ↔ DBAHA3L - 1 + C ₂ H ₄	6.00 10 ¹¹	0	12 978
18	DBAHA3L + C ₂ H ₃ ↔ DBAHA3L - 12 + C ₂ H ₄	6.00 10 ¹¹	0	12 978

¹k = ATⁿexp(-Ea/RT) with gas constant R in cal mol⁻¹K⁻¹

²Notations used for the different species are clarified in Figure 1

Figure captions

Figure 1: Molecules and radicals involved in Table 1

Figure 2: Mole fraction profiles of light species during acetylene pyrolysis at 1173 K and 8 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32].

Figure 3: Mole fraction profiles of first aromatic rings and light PAHs during acetylene pyrolysis at 1173 K and 8 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32].

Figure 4: Mole fraction profiles of heavy PAHs during acetylene pyrolysis at 1173 K and 15 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32]. * indicates a logarithmic scale in ordinate.

Figure 5: Mole fraction profiles of light species during ethylene pyrolysis at 1173 K and 8 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32].

Figure 6: Mole fraction profiles of first aromatic rings and light PAHs during ethylene pyrolysis at 1173 K and 8 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32].

Figure 7: Mole fraction profiles of heavy PAHs during ethylene pyrolysis at 1173 K and 15 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32]. * indicates a logarithmic scale in ordinate.

Figure 8: Main reaction pathways for benzene formation at 1173 K, 8 kPa and 1 s of residence time during: a) acetylene pyrolysis; b) ethylene pyrolysis. Percentages are related to the weight of the reaction in the formation of products.

Figure 9: Mole fractions of the EPA-PAHs obtained by modeling during acetylene, ethylene and propane pyrolysis at 1173 K, 15 kPa and a reactant conversion of 50%

Figure 10: Main reaction pathways for benzo[*a*]pyrene formation at 1173 K, 15 kPa and a reactant conversion of 50% during acetylene pyrolysis (percentages in bold) and ethylene pyrolysis (percentages in italic). Percentages are related to the weight of the reaction in the formation of products. Reaction pathways for naphthalene and indene formation are available in Supplementary data (S6).

Figure 11: Profiles of benzo[*a*]pyrene mole fraction obtained by modeling during acetylene, ethylene and propane pyrolysis at 1173 K and 15 kPa

Figure 12: Mole fractions of the EPA-PAHs divided by the mole fraction of acetylene obtained by modeling during acetylene and propane pyrolysis at 1173 K, 15 kPa and a residence time of 1 s

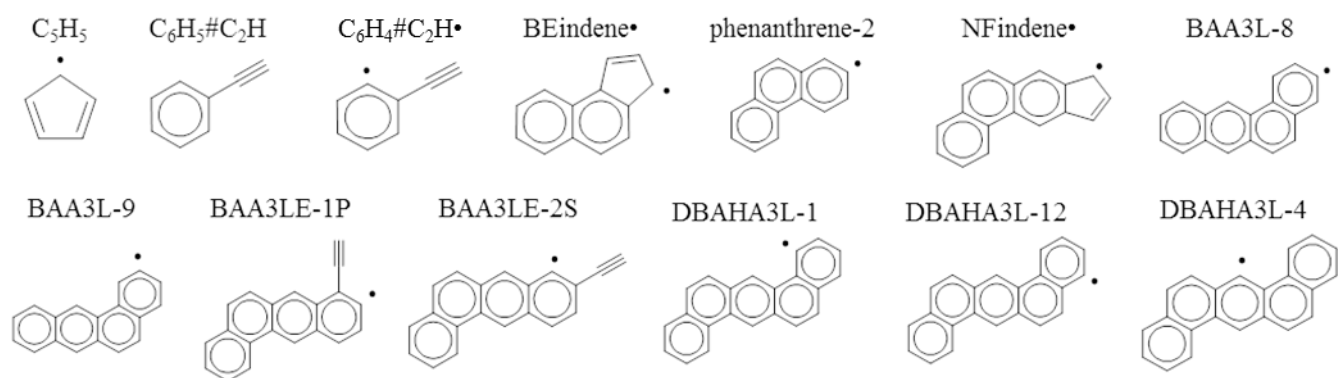


Figure 1: Molecules and radicals involved in Table 1

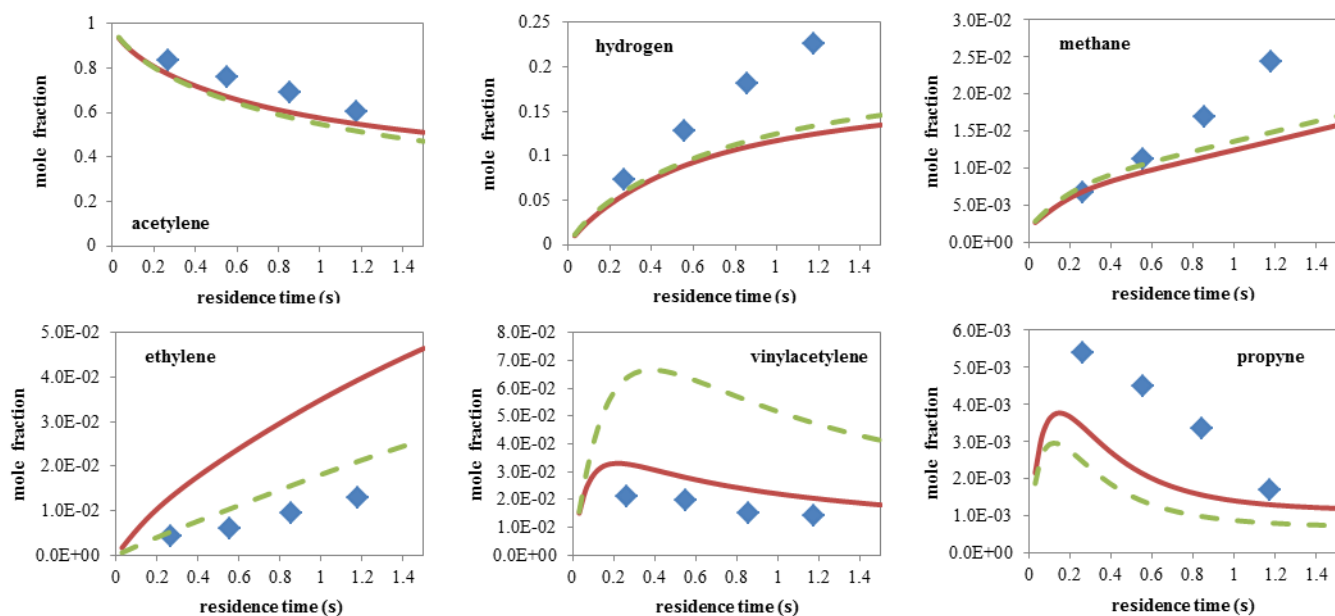


Figure 2: Mole fraction profiles of light species during acetylene pyrolysis at 1173 K and 8 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32].

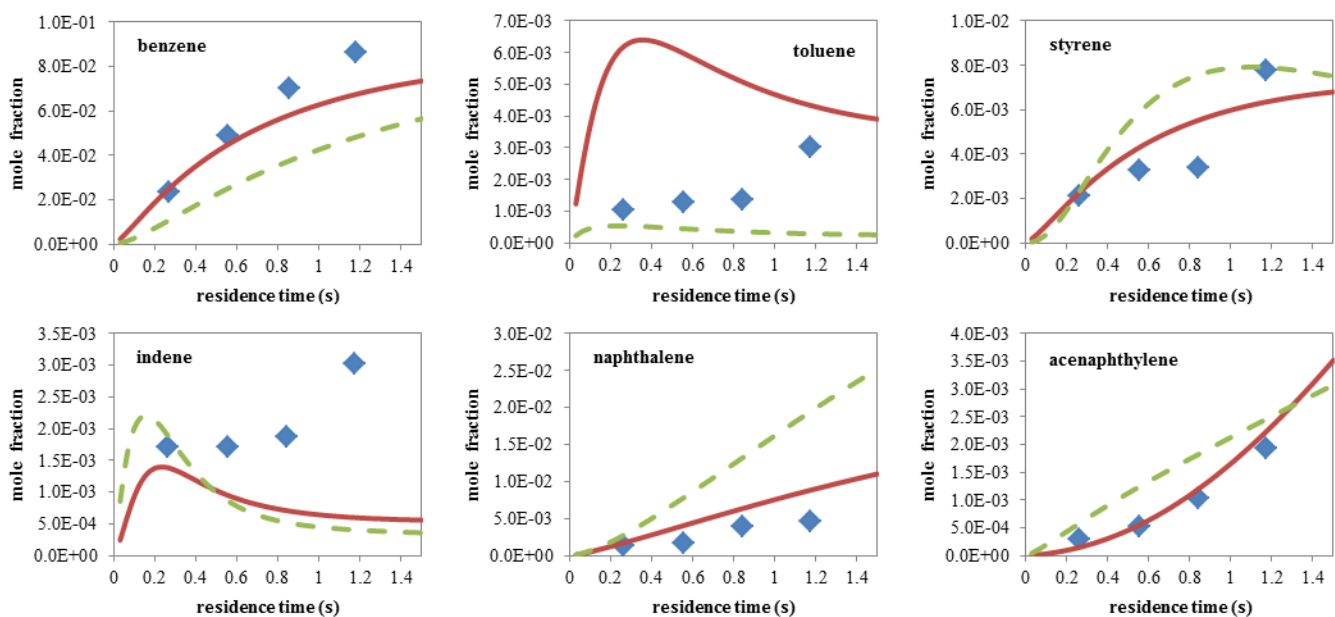


Figure 3: Mole fraction profiles of first aromatic rings and light PAHs during acetylene pyrolysis at 1173 K and 8 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32].

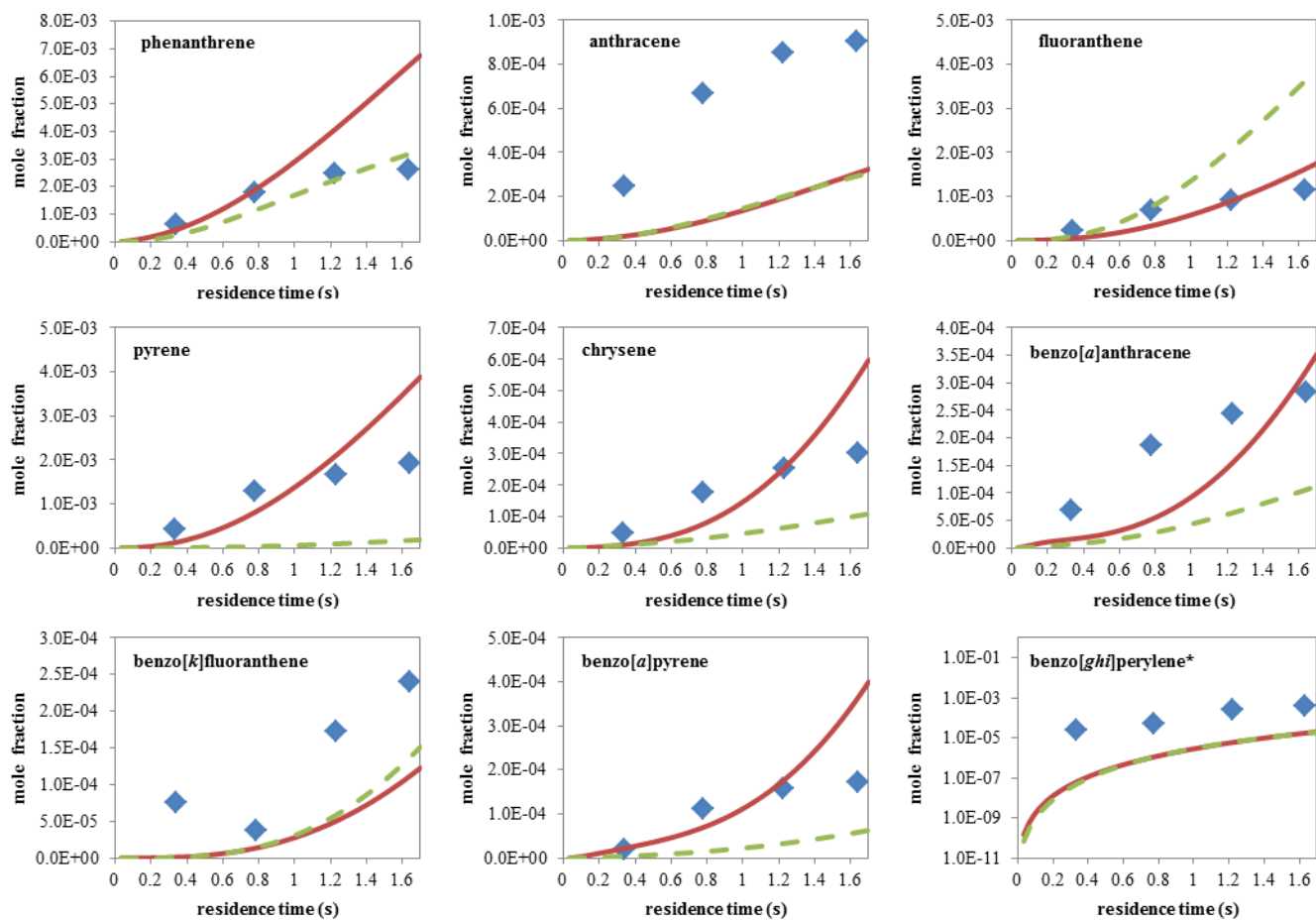


Figure 4: Mole fraction profiles of heavy PAHs during acetylene pyrolysis at 1173 K and 15 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32]. * indicates a logarithmic scale in ordinate.

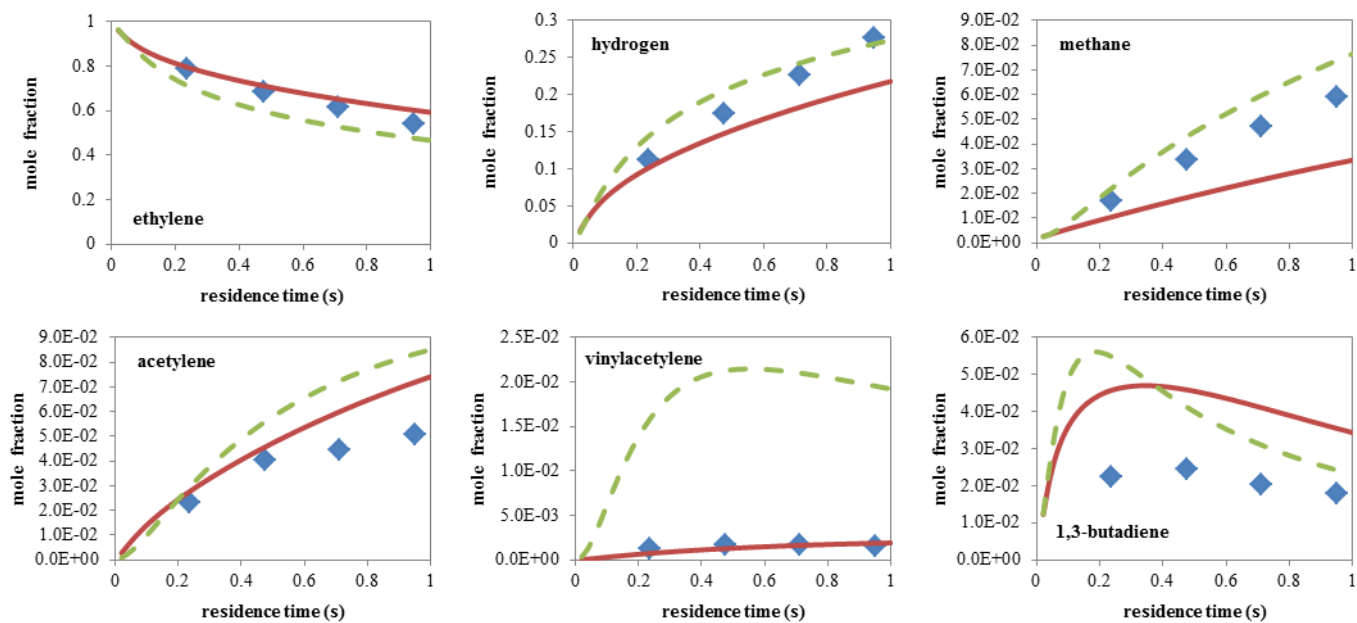


Figure 5: Mole fraction profiles of light species during ethylene pyrolysis at 1173 K and 8 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32].

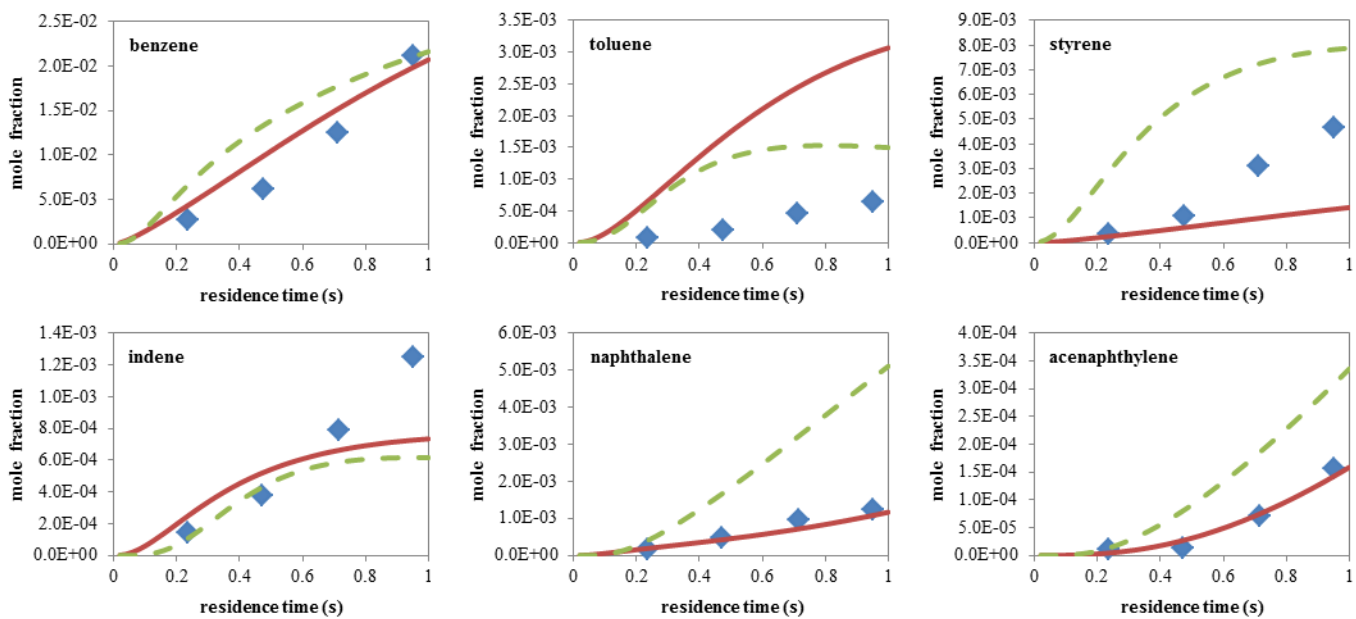


Figure 6: Mole fraction profiles of first aromatic rings and light PAHs during ethylene pyrolysis at 1173 K and 8 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32].

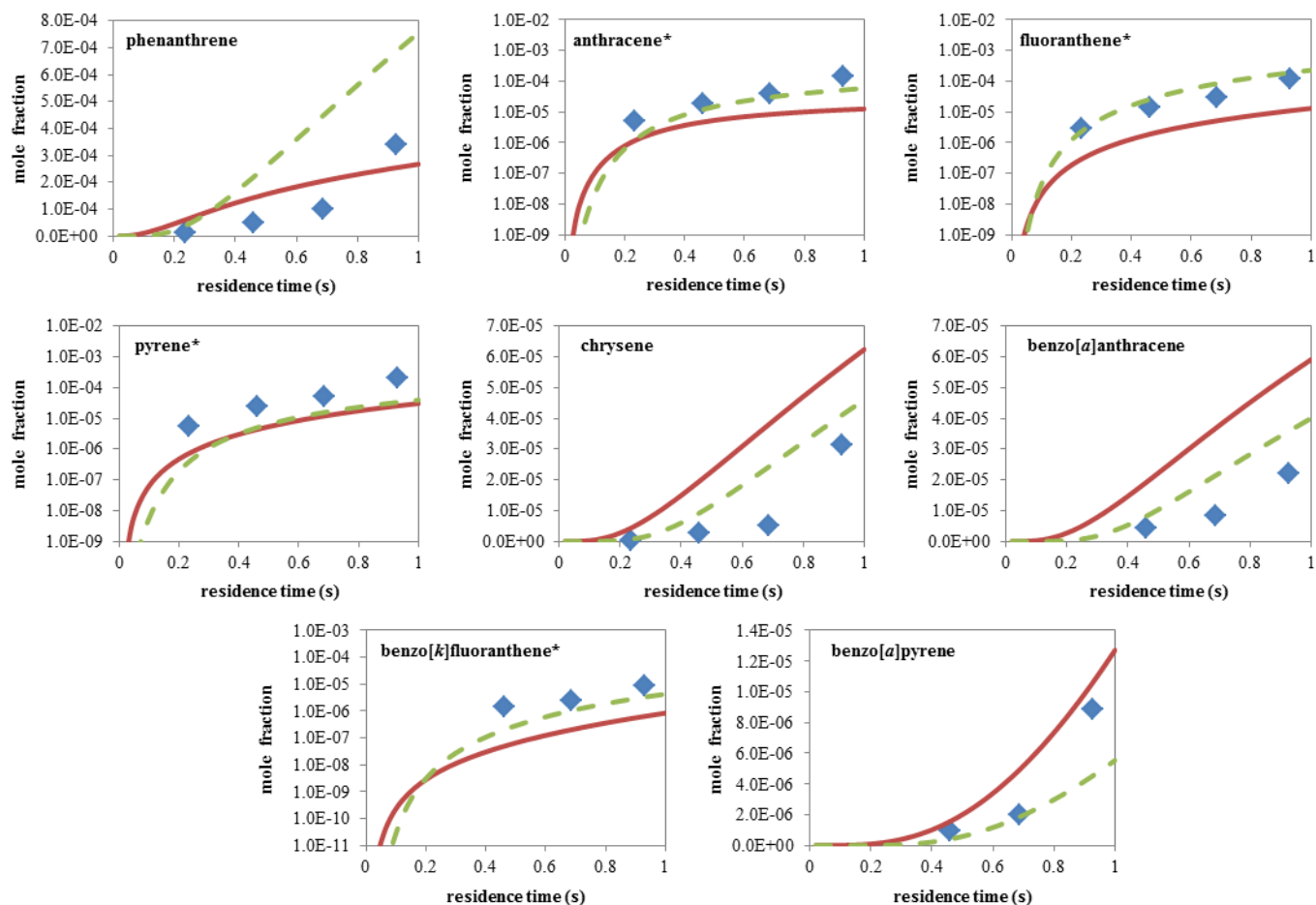


Figure 7: Mole fraction profiles of heavy PAHs during ethylene pyrolysis at 1173 K and 15 kPa. Points refer to experiments [31], solid lines to simulations and dashed lines to the model of Norinaga et al. [32]. * indicates a logarithmic scale in ordinate.

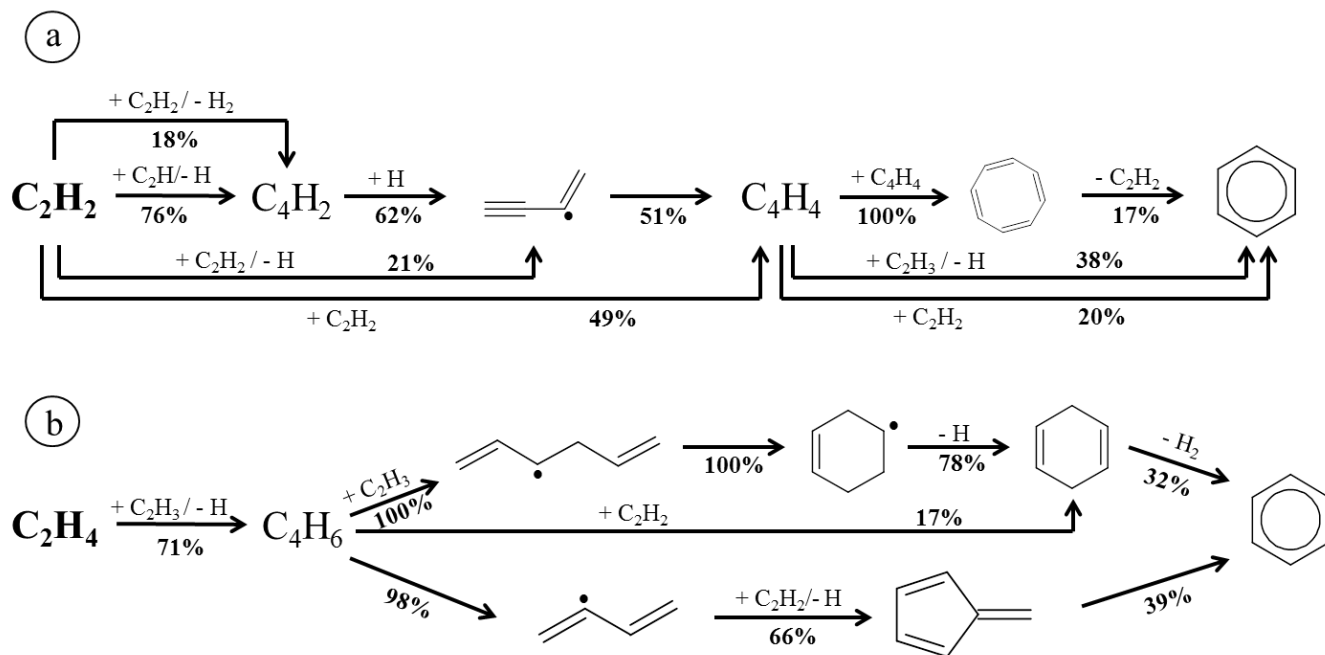


Figure 8: Main reaction pathways for benzene formation at 1173 K, 8 kPa and 1 s of residence time during: a) acetylene pyrolysis; b) ethylene pyrolysis. Percentages are related to the weight of the reaction in the formation of products.

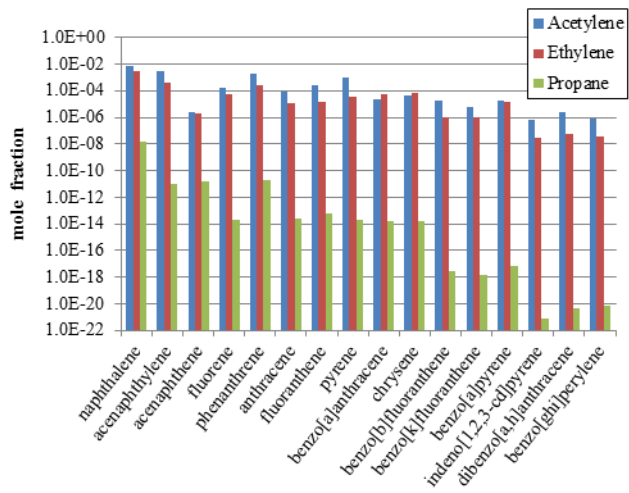


Figure 9: Mole fractions of the EPA-PAHs obtained by modeling during acetylene, ethylene and propane pyrolysis at 1173 K, 15 kPa and a reactant conversion of 50%

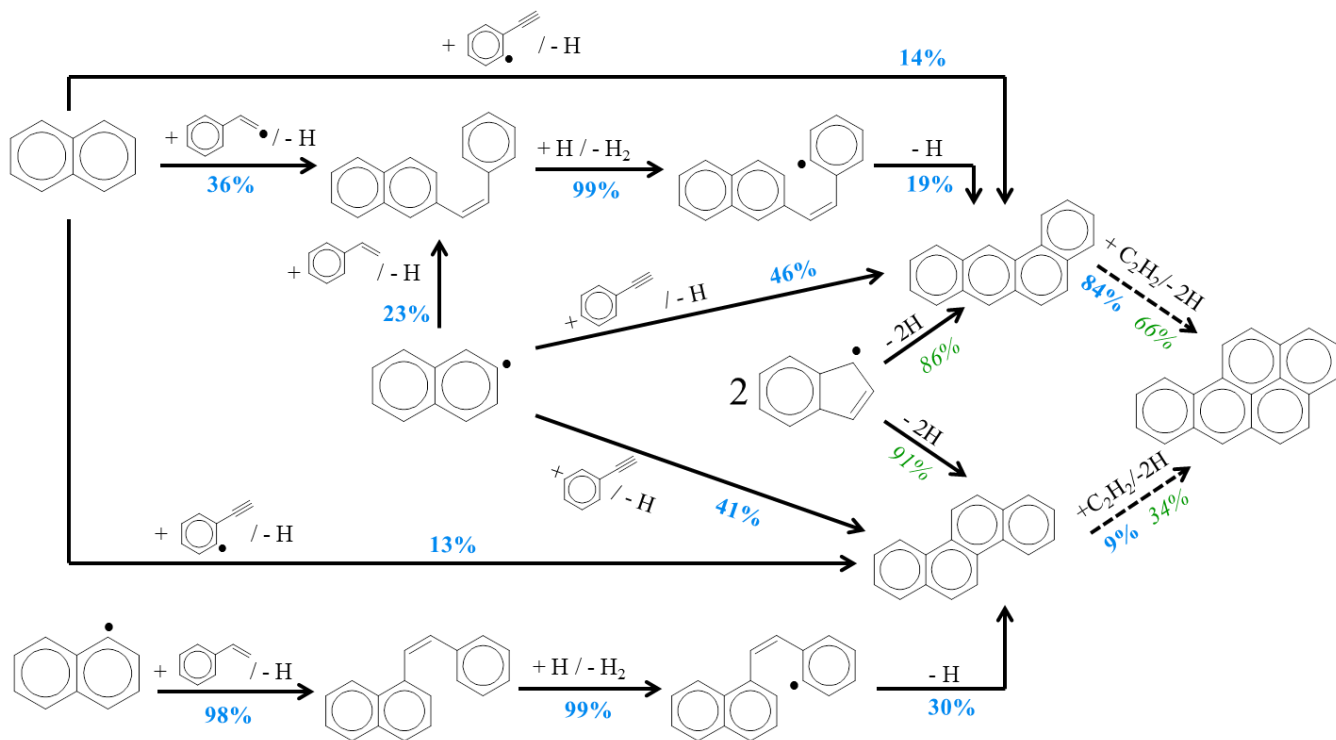


Figure 10: Main reaction pathways for benzo[*a*]pyrene formation at 1173 K, 15 kPa and a reactant conversion of 50% during acetylene pyrolysis (percentages in bold) and ethylene pyrolysis (percentages in italic). Percentages are related to the weight of the reaction in the formation of products. Reaction pathways for naphthalene and indene formation are available in Supplementary data (S6).

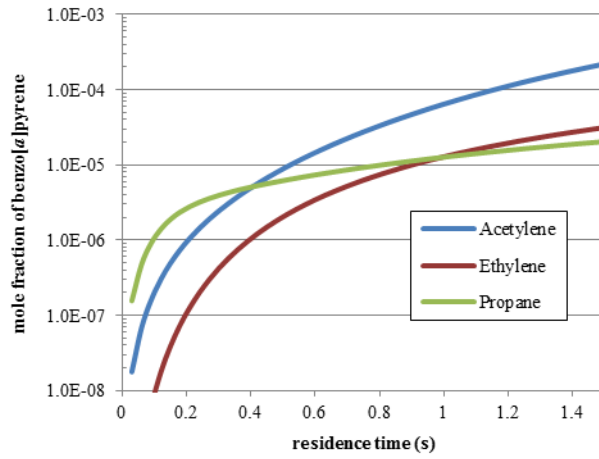


Figure 11: Profiles of benzo[a]pyrene mole fraction obtained by modeling during acetylene, ethylene and propane pyrolysis at 1173 K and 15 kPa

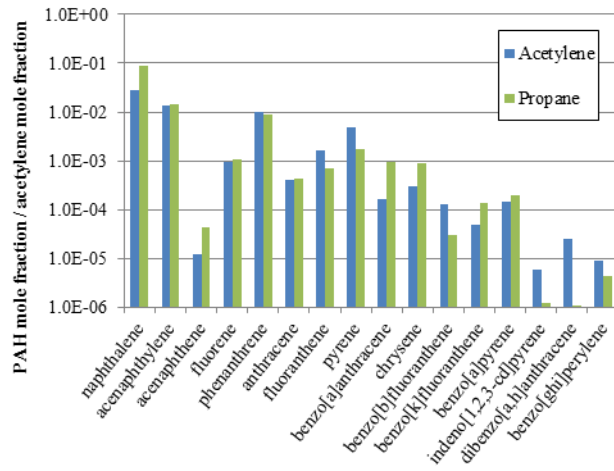


Figure 12: Mole fractions of the EPA-PAHs divided by the mole fraction of acetylene obtained by modeling during acetylene and propane pyrolysis at 1173 K, 15 kPa and a residence time of 1 s